(54) Title: FUEL CELL ANODE CONFIGURATION FOR CO TOLERANCE

(57) Abstract

A PEM fuel cell is designed to operate on a reformate fuel stream containing oxygen and diluted hydrogen fuel with CO impurities. A polymer electrolyte membrane (14) has an electrocatalyst (13) mixed with the polymer and bonded on an anode side of the membrane. An anode is formed of a porous electrically conductive material (12) and has a first surface abutting the layer of the polymer with the first electrocatalyst and a second surface facing away from the membrane. The second surface has a catalyst layer (18) effective to catalyze the oxidation of CO by oxygen present in the fuel stream. The layer of catalyst (18) is formed of a precious metal oxidation catalyst and a hydrophobic material that does not form an ionic conduction path between the layer of catalyst (18) on the second surface and the polymer electrolyte membrane (14).

FUEL CELL ANODE CONFIGURATION FOR CO TOLERANCE

BACKGROUND OF THE INVENTION

5   This invention relates to polymer electrolyte fuel cells, and, more particularly, to polymer electrolyte fuel cells suitable for operation with hydrogen reformate from a liquid fuel as a fuel gas. This invention was made with government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

10   Practical fuel cells based on perfluorinated ionomer membranes (e.g., Nafion™) use reformed fuel as a primary source for the anode feed material. The reformate, besides hydrogen, may contain trace amounts of carbon monoxide (CO, from a few to hundreds ppm), whose presence is detrimental to the cell performance. Energy conversion in fuel cells typically depends on highly

15   dispersed carbon-supported Pt , which catalyzes hydrogen electro-oxidation. However, CO strongly adsorbs on the Pt surface leading to a decrease of the Pt active surface area available for hydrogen oxidation, and, consequently, to losses in electrical current that are unacceptable for a practical device.

          There have been various approaches attempting to achieve full CO

20   tolerance in fuel cell performance. Full tolerance is typically defined as voltage losses no greater than 5% at any cell current in the presence of CO relative to that in its absence. For instance, binary or ternary Pt alloy-based catalysts have been tested. The other alloy metals act as promoters of CO electro-oxidation and stripping. However, not even the best known of these catalysts, such as Pt-Ru

25   alloys, are able to totally eliminate the detrimental effects of higher trace CO concentrations (>100 ppm) at 80 °C.

          A second direction has been to increase the cell operating temperature above 100 °C. In proton exchange membrane (PEM) fuel cells, this approach has been successful only for relatively short periods of time. At 120 °C, the sticking of

30   CO onto Pt decreases enough to maintain the hydrogen electro-oxidation rate without significant losses. But higher operating temperatures bring additional problems to ordinary PEM fuel cell, such as catalyst layer instability and ionomer membrane dehydration. These effects cause relatively rapid deterioration of the cell performance.

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A third approach is to bleed a small amount of air into the anode along with the fuel stream as described in U.S. Patent 4,910,099, issued May 20, 1990, to Gottesfeld, incorporated herein by reference. Oxygen from the air is able to oxidize the CO adsorbed on the catalyst layer to CO_2, which is released from the

5   catalyst. The air cleans Pt sites, making them available for H_2 electro-oxidation at an acceptable rate. Nevertheless, there are limits on how much air can be permitted into the cell without sacrificing fuel efficiency since oxygen in the air combines with the hydrogen fuel gas. Also, safety becomes an issue because of the potential explosive hazard presented by H_2/O_2 mixtures with increasing

10   amounts of O_2. These considerations indicate that injecting the minimum effective amount of air for a given content of CO is the most desirable condition for this approach.

       "Electrocatalysis Issues in Polymer Electrolyte Fuel Cells," Wilson et al.,IECEC Conference Proceedings, 1.1203-1.1208 (1993), reported difficulties in

15   achieving CO tolerance with "thin-film" catalyst membrane layers with air injection. Thin film catalyst membrane layers are described in U.S. Patents 5,211,984, issued May 18, 1993, and 5,234,777, issued August 10, 1993, both to Wilson and incorporated herein by reference. The membrane catalysts described therein typically have lower Pt loadings on the order of 0.15 $mgPt/cm^2$ in the anode and

20   are prepared so that all catalyst particles are very effectively coated with recast ionomer for incorporation onto a membrane surface. Addition of a Pt-catalyzed carbon paper upstream from the cell (called "pre-filter" in the 1993 paper), provided good CO oxidation activity when oxygen, or air, was added to the hydrogen stream. Such activity was then comparable to that found with

25   commercial ETEK electrodes ('099 Patent) in terms of overall Pt loading and level of air bleed required at given CO impurity level.

       The present invention recognizes that the Wilson results suggest that the additional small amount of Pt catalyst that is uncoated by ionomer upstream from the cell provides effective oxidation of CO and, thus, enables effective

30   electrochemical anode activity at the thin-film catalyst that is bonded to the anode side of the membrane. We have recognized that the proper approach is to divide the CO oxidation and hydrogen electrooxidation functions between two components of the anode catalyst. One component would be devoted to CO

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chemical oxidation by O_2 and the other to electrooxidation of hydrogen on an anode catalyst "free of CO contamination threats".

Implementing such an approach effectively is a sensitive function of the composition of the fuel feed stream and the other important requirements of PEM fuel cell stack and system technology. Such requirements would typically be to achieve complete removal of CO at the highest possible CO level in an otherwise realistic fuel stream composition. In addition, this would be achieved with minimum air bleed levels, to avoid excessive fuel loss, and with the lowest possible overall Pt loadings to achieve the demanding cost targets and at an operating temperature of 80 °C or less.

U.S. Patent 5,482,680, issued January 9, 1996, to Wilkinson et al., generally describes the application of a "selective oxidizer" to oxidize CO in a reformate fuel stream upstream from the fuel cell anode. In one embodiment shown in Figure 15, Wilkinson teaches a selective oxidizing catalyst layer disposed on the surface of the anode facing away from the electrolyte membrane. The anode is formed of porous electrically conductive sheet material with a layer of electrocatalyst disposed on the surface facing the membrane. The only oxidation catalyst described by Wilkinson is a mixture of 75% platinum/25% rhodium to oxidize CO present in the fuel stream. There is no teaching about application of such an anode to the catalyzed membrane of the '984 and '777 patents and there are no teachings about how to form the anode structure to avoid excessive fuel loss, provide cost effective catalyst loadings, and provide the removal of CO concentrations typically found in reformate fuel streams.

It should be realized that significantly higher challenges are presented by the type of anode feed described and the high fuel utilization demanded herein vs. the description of the" air bleeding technique " of the '099 patent for CO poisoning elimination. Firstly, 100 ppm CO in a gas mixture which is only 40% hydrogen (a typical gasoline reformate fuel stream) is equivalent to 250 ppm of CO in neat hydrogen in terms of the poisoning effect expected. This is because the pressure ratio $P_{CO} / P_{hydrogen}$ determines the CO competition for the catalyst surface . Complete elimination of 250 ppm CO in neat hydrogen, at the desired cell operating temperature of 80°C, has not been demonstrated before. Additionally, two important targets for practical fuel cells are to keep the total Pt

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anode loading below 0.5 mg/cm^2 (to limit cost) and to keep the air bleed level

below 5% of total anode flow to minimize fuel loss and safety concerns.

The present invention addresses the problem of reducing the level of CO in

reformate fuel gas to acceptable levels and novel features of the invention will be

5   set forth in part in the description which follows, and in part will become apparent

to those skilled in the art upon examination of the following or may be learned by

practice of the invention. The objects and advantages of the invention may be

realized and attained by means of the instrumentalities and combinations

particularly pointed out in the appended claims.

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SUMMARY OF THE INVENTION

To achieve the foregoing and other objects, and in accordance with the

purposes of the present invention, as embodied and broadly described herein, the

apparatus of this invention may comprise a PEM fuel cell designed to operate in a

15   reformate fuel stream containing diluted hydrogen fuel with CO as an impurity and

with added air. A polymer electrolyte membrane has an electrocatalytic surface

formed from an electrocatalyst mixed with the polymer and bonded on an anode

side of the membrane. An anode is formed of a porous electrically conductive

material and has a first surface abutting the layer of the polymer with the first

20   electrocatalyst and a second surface facing away from the membrane. The

second surface has a catalyst layer effective to catalyze the oxidation of CO by

oxygen present in the fuel stream. The layer of catalyst is formed of a precious

metal oxidation catalyst and a hydrophobic material that does not form an ionic

conduction path between the layer of catalyst on the second surface and the

25   polymer electrolyte membrane.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of

the specification, illustrate the embodiments of the present invention and,

30   together with the description, serve to explain the principles of the invention. In

the drawings:

FIGURE 1 is an exploded cross-section of one embodiment of a CO

tolerant fuel cell according to the present invention.

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FIGURE 2 depicts polarization curves of a fuel cell with a standard anode configuration.

FIGURE 3 depicts polarization curves of a fuel cell with a reconfigured anode.

FIGURE 4 depicts polarization curves of a fuel cell with a second standard anode.

FIGURE 5 depicts polarization curves of a fuel cell with a second reconfigured anode.

FIGURE 6 depicts anode overvoltage curves with a standard anode.

FIGURE 7 depicts anode overvoltage curves with a reconfigured anode formed by sputtering Pt the anode backing.

FIGURE 8 depicts anode overvoltage curves with a reconfigured anode formed from a Pt-catalyzed cloth anode.

FIGURE 9 depicts anode overvoltage with the cell shown in FIGURE 8 with a variety of fuel compositions.

FIGURE 10 depicts a polarization curve with a reconfigured anode with various fuel compositions.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, shown in Figure 1, an anode is based on a catalyzed membrane 14 prepared according to the LANL thin-film catalyst technology described in the '984 and '777 Wilson patents, *supra*, with an adjacent backing layer 12 that contains additional catalytic sites for effective CO oxidation. As described by the '984 and '777 Wilson patents, membrane electrode assembly (MEA) 13, 14, 15 is prepared by application of Pt/C, or Pt alloy/C catalyst 13 to one side of ionomeric membrane 14 (anode catalyst) and a Pt/C catalyst 15 to the other side of membrane 14 (cathode catalyst). Using the TBA$^+$ form of the recast ionomer for preparation of the catalyst layer and the Na$^+$ form of the membrane allows effective hot-pressing for bonding the catalyst layer to the membrane as described in the Wilson patents. This preparation is important for achieving both high utilization and long term stability for anode catalyst 13. It will be understood that catalyst layers 13 and 15 are not separate structures, as shown in Figure 1 for clarity, but are integral with membrane 14.

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Low loadings of catalyst 13 bonded to the anode side of membrane 14 (typically, 0.2 mgPt/cm^2 or less) in this way, enable effective operation with 100 ppm CO in reformate in conjunction with the anode structure described below. Reformate fuel gas is input through gas manifold 11 and air (oxygen) is input through gas manifold 19.

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Anode backing layer 12 is used to provide the additional component of anode catalyst for effective CO oxidation. Backing layer 12 has the following properties:

* Contains extra Pt catalyst 18 not coated by ionomer, thus making catalyst

10   sites easily available to both CO and O$_2$ molecules in the gas phase.

* Exhibits overall gas transport properties similar to those of ordinary, uncatalyzed backing layers used to date adjacent the catalyzed membrane.

* Exhibits good hydrophobic characteristics to prevent "flooding" of the

15   backing in the presence of the high level of humidification required to achieve high conductivity in anode catalyst layer 13 (high humidification of the fuel feed stream is required to minimize losses in an anode operating with dilute hydrogen feed streams).

Backing layer 12, 18 thus produced has a fraction of catalyst which is not

20   active for the electrochemical fuel cell reaction since it is deposited without allowing a continuous ionic conduction path to the rest of catalyst 13 bonded to membrane 14. In this way the CO-contaminated H$_2$, which also contains a small amount of O$_2$ (from air bleeding), will first encounter outer catalyst layer 18. Layer 18 will promote the direct chemical oxidation of the CO with O$_2$, before the fuel

25   stream reaches internal catalyst layer 13 where the electrochemical oxidation of H$_2$ takes place. In other words, outer layer 18 acts to reduce the CO concentration to levels that will not poison the Pt surface in internal catalyst layer 13.

In an experimental embodiment, E-TEK carbon cloth 12 (300 micrometer

30   thick) was filled on one side only with carbon powder/PTFE paste, followed by sintering at 350°C to yield a 50 micrometer thick layer of PTFE-bonded carbon. An ordinary E-TEK backing layer comprises a carbon cloth filled on both sides with 50 micrometer thick PTFE-bonded carbon powder layers for electrical

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conductivity. The one-side-filled E-TEK carbon cloth 12 leaves the other side available for application of a PTFE-bonded Pt/C catalyst. Pt/C catalyst (20 wt% Pt) was mixed with PTFE and applied to the second side of the one-side- filled E-TEK carbon cloth, at a total loading of 0.20-0.25 $mgPt/cm^2$. The final thickness of this catalyst layer 18 (50 micrometer), and concomitant gas transport properties were the same as those of the uncatalyzed PTFE-bonded carbon layer in an uncatalyzed carbon cloth. This configuration therefore achieves the combined required properties of the backing layer, namely a catalyst of high activity for oxidation of CO by oxygen in added air while maintaining the transport properties and hydrophobic characteristics of an ordinary backing.

Three procedures of preparing outer catalyst layer 18 on backing material 12 have been provided: 1) painting a hydrophobic Pt/carbon layer onto the backing. 2) using Pt-sputtered carbon cloth, and 3) using a commercial Pt-catalyzed carbon cloth. These modes are described as follows:

Procedure 1: Pt/C/Teflon catalyst composite layer painted onto the backing:

Typical ink contents: 0.7 g 20% Pt on Vulcan XC-72 (ETEK™), 3.5 ml "Teflon 120" suspension (0.02 g solids/ml water), 0.8 g glycerol, 5 ml isopropanol and, 2.0 ml water. The ink can also be prepared with 30% Pt-Ru alloy on Vulcan XC-72 (ETEK™).

Ink and layer preparations: The mixture was sonicated for 10 minutes and then bar-stirred overnight. The ink was brush painted onto a pre-weighed piece of carbon cloth (ETEK™ uncatalyzed carbon cloth) and let dry in the air for 30 min. Then the catalyst-painted cloth was sintered in the air at 280 °C for 15 minutes. A catalyst layer with good adherence to the cloth is obtained. The "Teflon 120" copolymer in the composite acts as binder and also provides a hydrophobic surface needed for proper water management at the anode during cell operation. Also, heating at 280 °C eliminates water, isopropanol and glycerol, so a typical final composition of the dry layer is 18% Pt, 74% carbon black and 8% "Teflon 120".

Procedure 2: Pt-sputtered carbon cloth: A piece of uncatalyzed carbon cloth (ETEK) was sputtered with an approximately 200 Å thick Pt layer,

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using conventional sputtering techniques. The corresponding precious metal loading is about 0.05 mg Pt/cm^2.

Procedure 3: Proprietary Pt catalyzed carbon cloth: A proprietary 20% Pt/carbon carbon cloth was also tested as a backing material (purchased from ETEK™). This backing contains 0.35 mg Pt/cm^2 in a surface layer about 50 μm thick and was used as received.

When the cell is put together, the catalyzed side 18 of carbon cloth 12 is positioned adjacent the gas flow channels 11 and the side with uncatalyzed, PTFE-bonded carbon powder is adjacent the catalyst layer bonded to membrane 14. The former side thus facilitates $CO + O_2$ reactivity whereas the latter side serves to prevent significant accumulation of liquid water ("flooding") near the electrochemically active anode catalyst.

Experimental Cells 1-8 were formed with catalyst (chemical 18 and electrochemical 13) distributions as shown in Table A.

TABLE A

Cell ID	Catalyst	Membrane 13 (mg/cm^2)	Backing 18 (mg/cm^2)
1 (Fig. 2)	Pt/Ru	0.71	---
2 (Fig. 3)	Pt/Ru	0.31	0.32
3 (Fig. 4)	Pt	0.46	---
4 (Fig. 5)	Pt	0.18	0.29
5 (Fig. 6)	Pt/Ru	0.37	---
6 (Fig. 7)	Pt/Ru Pt sputtered	0.33	0.05
7 (Figs. 8, 9)	Pt/Ru Pt-catalyzed cloth	0.40	0.35
8 (Fig. 10)	Pt Pt/Ru	0.13	0.32

The cathode catalyst loading was a Pt catalyst in the range of 0.15-0.20 mg/cm^2.

As shown by Figures 2-10, the distribution of catalyst between the membrane (electrocatalyst) and the backing (oxidation catalyst) provides effective operation with CO at concentrations up to the equivalent of 250 ppm CO in neat H_2 with only 1% to 6% by volume of air in the fuel stream and with total catalyst loadings of less than about 0.75 mg/cm^2. While both Pt/Ru and Pt catalysts are

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shown to be effective, the preferred catalyst is Pt from both performance and lifetime considerations.

Figures 2 and 3 compare the performance of two cells (standard and reconfigured anodes) with equivalent total anode catalyst loading (c.a. 0.6-0.7 mg metals/cm^2), fed with various fuel compositions. In both cells the catalyst at the membrane contained carbon-supported Pt-Ru.

Comments 1 : Comparison of Figs. 2 and 3 clearly demonstrates that:

a) 100 ppm of CO in the fuel practically ruins the performance in both cells.

b) Cell No. 2, with a reconfigured anode, needs only 1% of air bleeding to recover a performance almost as good as that with neat H$_2$. For cell No.1 even with 10% air bleeding, the recovery is far from complete.

Figures 4 and 5 compare the performance of two cells (standard and reconfigured anodes) with equivalent total anode catalyst loading (c.a. 0.5 mg Pt/cm^2), fed with various fuel compositions. In both cells the catalyst at the membrane contained carbon supported Pt.

Comments 2: Comparison of Figures. 4 and 5 shows that:

a) Like the previous cells, 100 ppm of CO in the neat H$_2$ fuel stream virtually ruins the performance of both cell Nos.4 and 5.

b) Cells 3 and 4, whose anodes contained only Pt (either with standard or reconfigured distribution), gave much better overall performance than those cells with Pt-Ru at the internal catalyst layer (Cells 1 and 2). An additional advantage of Pt-only catalysts is the fact that they appear to sustain long term (thousand hours) performance with only minor losses. Pt-Ru alloys performances decrease somewhat faster.

c) With 2% air bleeding cell No.3 with an ordinary anode partially recovered; however the losses were still considerable.

d) With 2% air bleeding, cell No. 4 with the reconfigured anode showed practically full performance recovery.

In general with neat H$_2$, catalysts with Pt only at membrane catalyst layer 13 exhibit significantly better overall performances than equivalent loadings of Pt-Ru alloys. With CO contaminated fuels (e.g. reformate), the alloys are more tolerant. However, with 1 to 2% air bleeding the advantage goes back to Pt-only catalysts.

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In summary, reconfigured anodes with Pt catalysts used with air bleeding for CO tolerance clearly show superior performance over (a) anodes with PtRu catalysts with or without air bleed, and, (b) over ordinary anode structures with the same total Pt loading.

5 Pt-sputtered backings (procedure 2) as reconfigured anodes also showed enhanced CO tolerance when compared to standard anodes with equal catalysis loadings.

A different way to present the results is to calculate from polarization curves the difference between the cell voltage (at a given current density)

10 obtained with neat H_2 and that with any other fuel gas mixture. This difference is known as "anode excess overvoltage", because it is a voltage loss originating at the anode due to the presence of CO. The smaller the excess overvoltage the better the tolerance to CO.

Figures 6 and 7 compare CO tolerance of a standard anode cell with a cell

15 whose anode backing contained a Pt-sputtered carbon cloth (Procedure 2). Again, total catalyst loadings are practically the same for the ordinary and reconfigured anodes.

Comments 3: Cell No.6 (reconfigured anode) showed tolerance to 100 ppm CO with 6% air bleed. The standard cell No.5 (with an equivalent anode

20 catalyst loading) was not tolerant to this amount of CO even with 14 % air bleeding.

Reconfigured anodes including commercial Pt-catalyzed backings (procedure 3) were also tested for CO tolerance with air bleeding. The results are shown in Figure 8.

25 Comments 4: Figure 8 shows that Cell No.7 with a reconfigured anode was fully tolerant (no overvoltage) to 100 ppm CO with 6% air. This result can be compared to that of cell No.1 (Figure 2), which also has a Pt-Ru catalyst bonded to the anode side of the membrane, where even with 10% air the anode overvoltages generated by the CO presence in the fuel are very large. Notice

30 again that the anode total precious metal loadings in both of these cells are very similar.

Reformate fuel feeds may contain a large amount of carbon dioxide (typically 25%). Reconfigured anodes were tested with air bleed to determine if

the presence of CO_2 may have some negative effect on cell performance. The results are shown in Figure 9.

Comments 5: As shown by the lower curve in Figure 9, the presence of 25% of CO_2 in the anode fuel feed does not have a significant effect on the cell performance. A high concentration of CO_2 and H_2 could favor the inverse of the water-gas shift reaction ($CO_2+H_2 \rightarrow CO + H_2O$) and produce enough CO to totally poison the catalyst. The result above shows that, if any CO is formed in this way, it is completely and effectively oxidized in the reconfigured anode by the air bleed. The cell also showed tolerance to 100 ppm of CO added to the CO_2 + H_2 mixture, with 6% air bleeding.

Figure 10 shows polarization curves of a cell operating with a simulated reformate fuel containing 40% H_2, 35% N_2, 25% CO_2 and 100 ppm CO. The reformate mixture was prepared from pure gases.

Comments 6 :

Fig. 10 shows the performance of cell No. 8 with a reconfigured anode operating on reformate fuel containing 100 ppm CO. With this reformate mixture the cell performance is poor. However, it almost fully recovers if 2% air is bled in the fuel stream. With 4% air the performance is as good as with neat H_2. The full effectiveness of the reconfigured anode is reflected by Figure 10, because the hydrogen feed stream is very diluted (40%).

The result of such dilution is that high anode backing transport properties have to be achieved and, at the same time, the 100 ppm CO--equivalent in poisoning effect to 250 ppm in neat H_2--have to be effectively oxidized by air bleed at low overall catalyst loading. It is the effective distribution of Pt catalyst in the reconfigured anode and the way the backing layer is minimally perturbed by the portion of Pt acting as CO oxidation catalyst, that provide the desirable combination of (a) minimal effects of hydrogen dilution and (b) highly effective removal of CO at low levels of air bleed with low catalyst loadings.
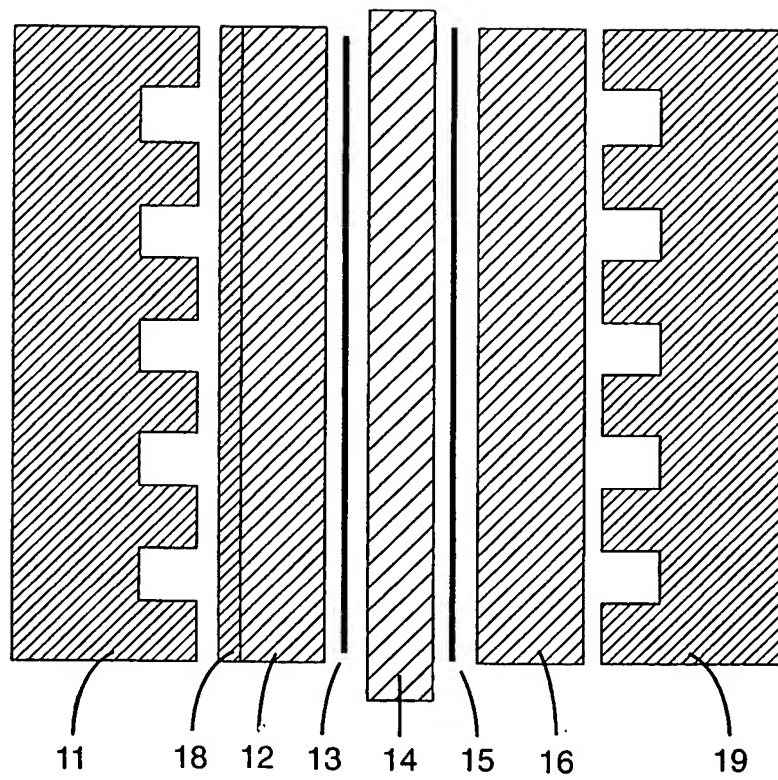
Notice that cell No. 8 contains a Pt-Ru alloy as the catalyst in the anode backing. This result shows that Pt-Ru based catalysts at the anode backing are also effective in enhancing CO tolerance with air bleeding.

The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to
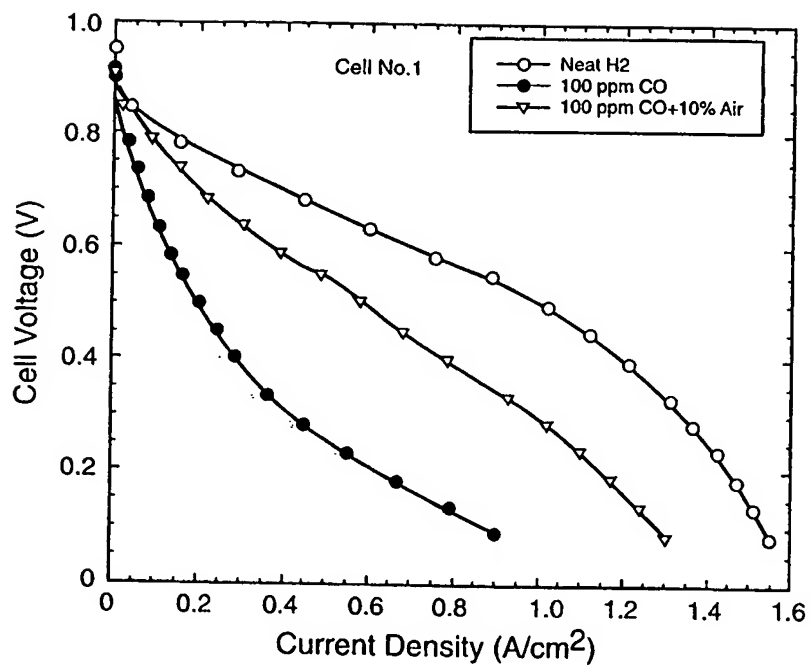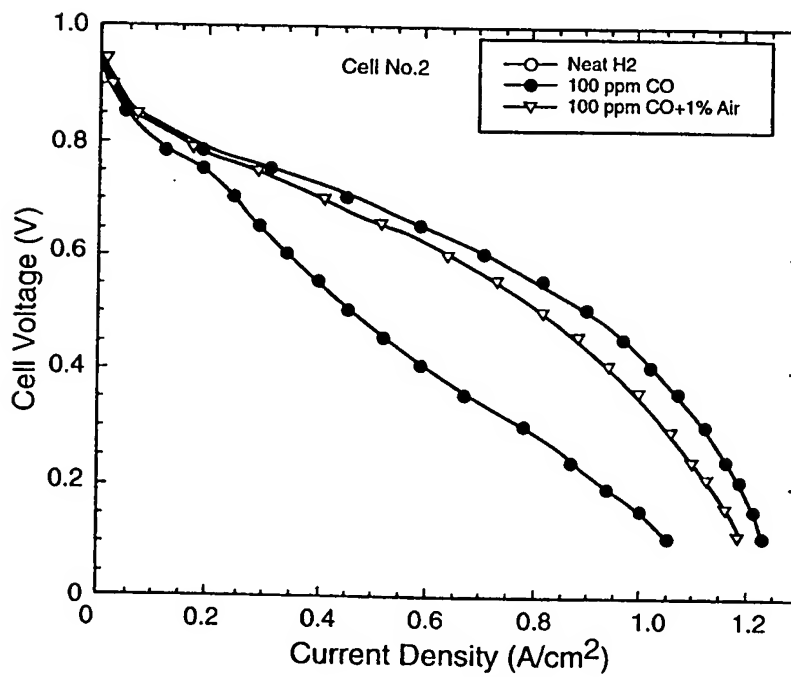
12

limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the

5   invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.
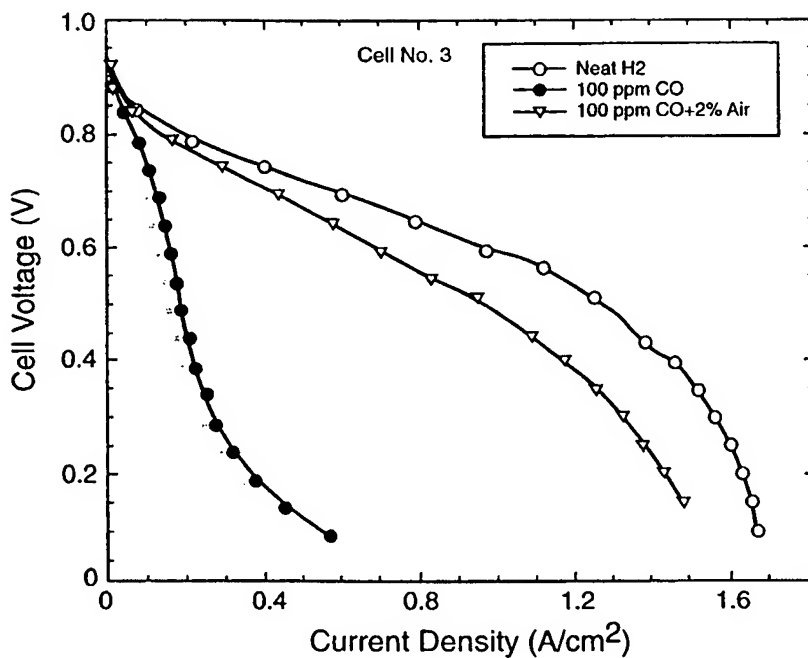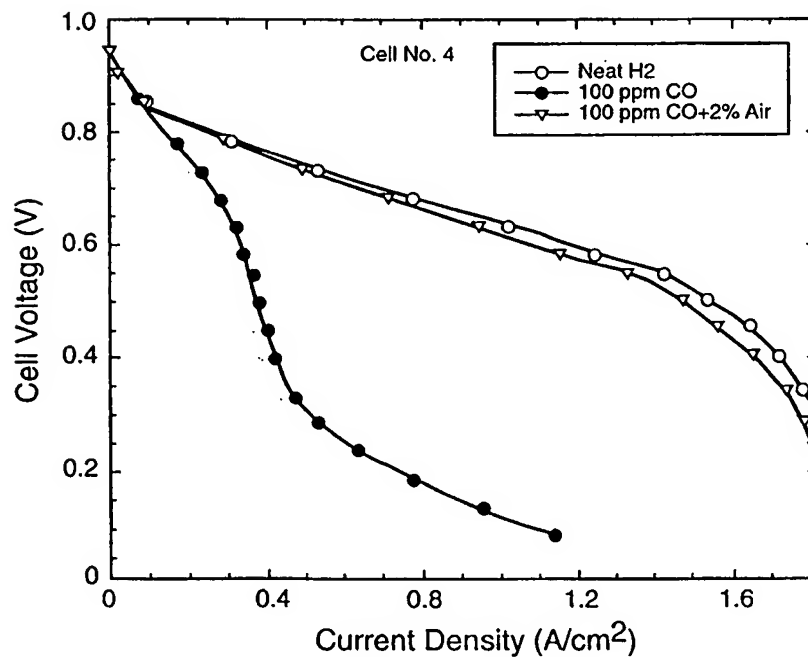
13

WHAT IS CLAIMED IS:

1.   A PEM fuel cell comprising:

a reformate fuel stream containing diluted hydrogen fuel with CO as an impurity and with added air;

a polymer electrolyte membrane having an electrocatalytic surface formed from an electrocatalyst mixed with said polymer and bonded on an anode side of said membrane; and

an anode formed of a porous electrically conductive material and having a first surface abutting said electrolcatalytic surface and a second surface facing away from said membrane, where said second surface has a catalyst layer effective to catalyze the oxidation of CO by oxygen present in said fuel stream where at least said layer of catalyst is formed of a precious metal oxidation catalyst and a hydrophobic material that does not form an ionic conduction path between said layer of catalyst on said second surface and said polymer electrolyte membrane.

2.   A PEM fuel cell according to Claim 1, where said electrocatalyst is selected from the group consisting of Pt and Pt/Ru alloy and said oxidation catalyst is selected from the group consisting of Pt and Pt/Ru alloy.

3.   A PEM fuel cell according to Claim 1, wherein said electrocatalyst and said oxidation catalyst are Pt.

4.   A PEM fuel cell according to any one of Claims 1, 2, and 3, where the total loading of said electrocatalyst and said oxidation catalyst is less than about 0.75 mg/cm^2.

5.   A PEM fuel cell according to Claim 4, where said fuel stream has an air concentration of 1% to 6% by volume.

6.   A PEM fuel cell according to Claim 5, wherein said CO has a concentration up to a concentration equivalent to 250 ppm CO in neat hydrogen.
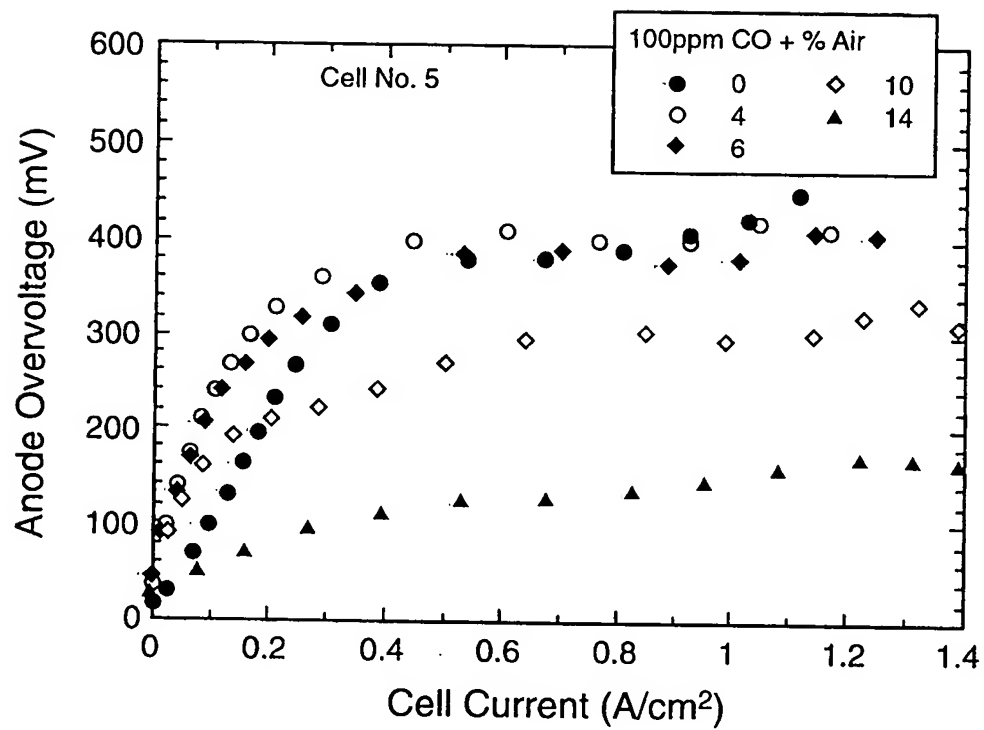
Fig.1

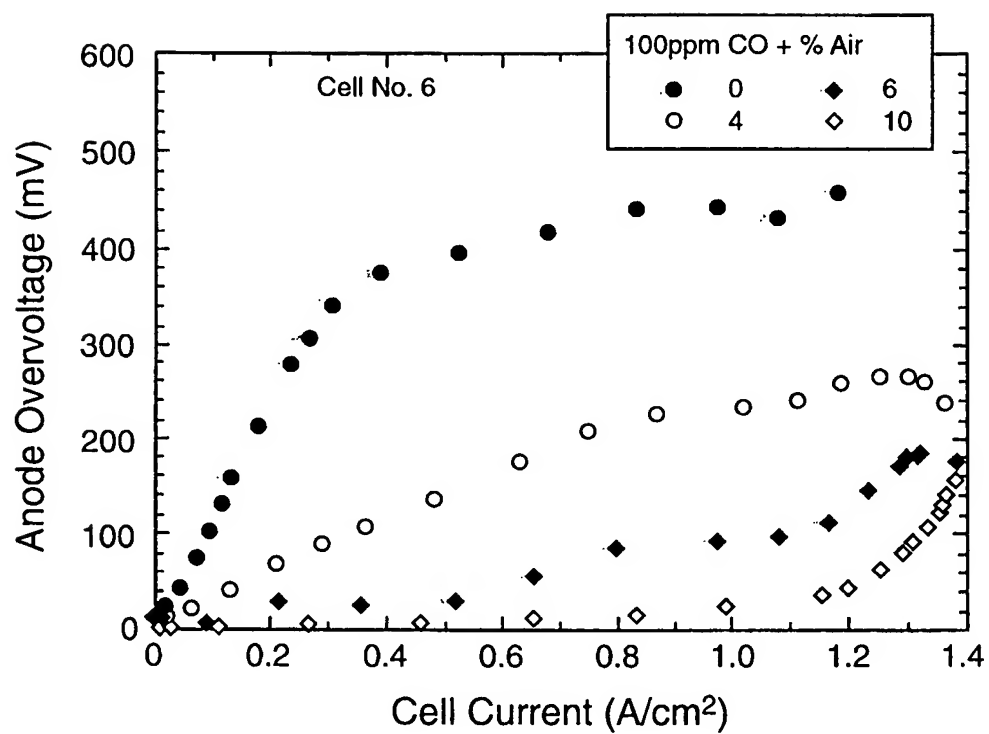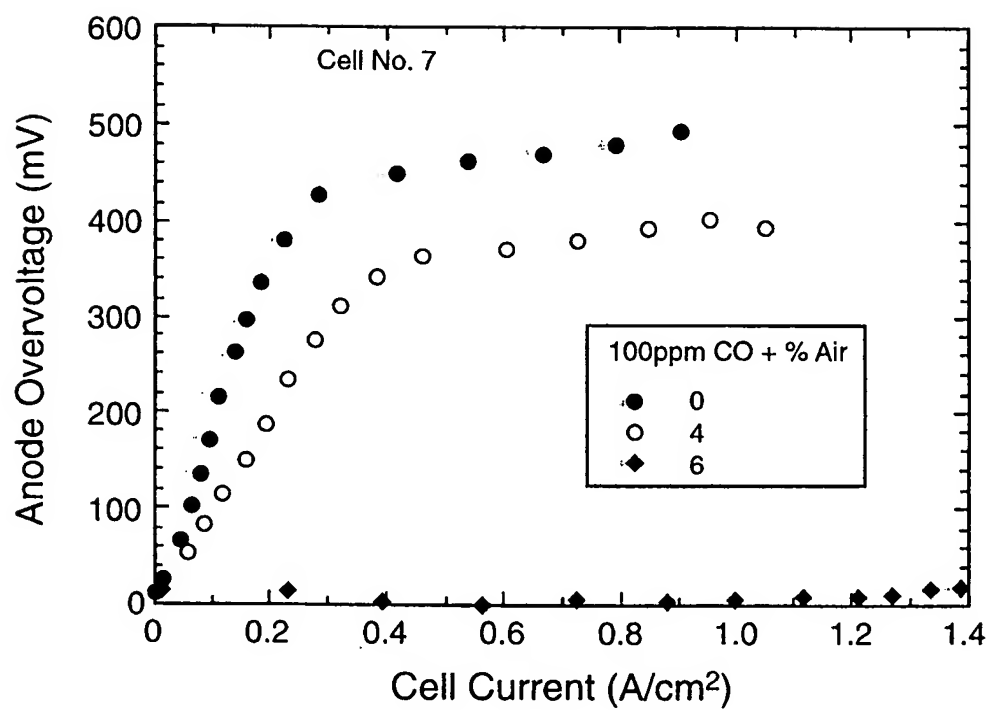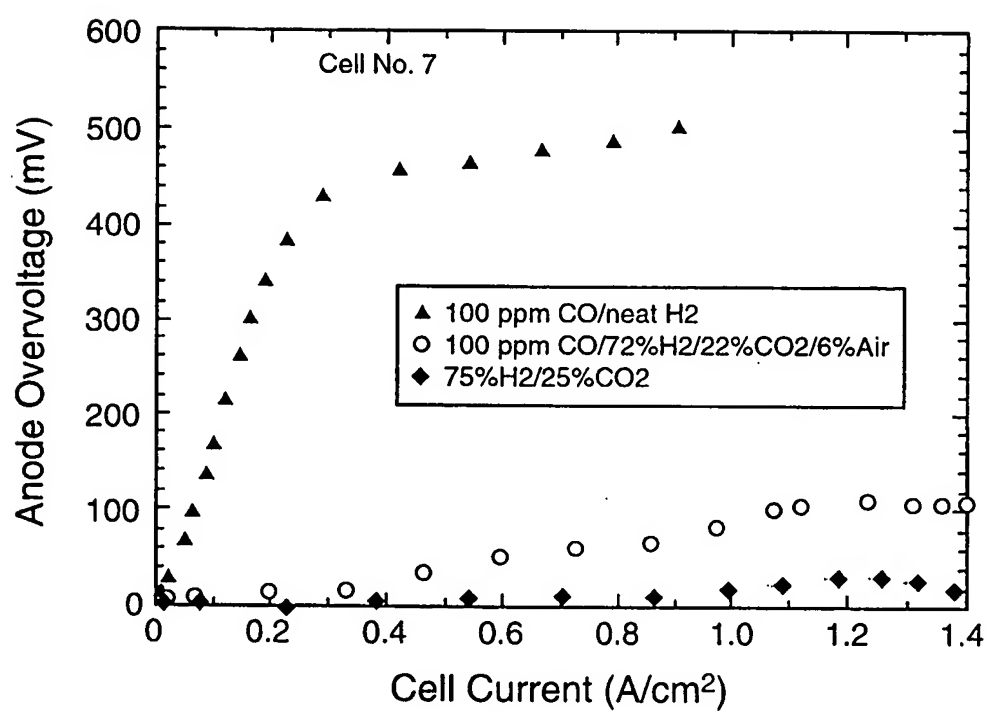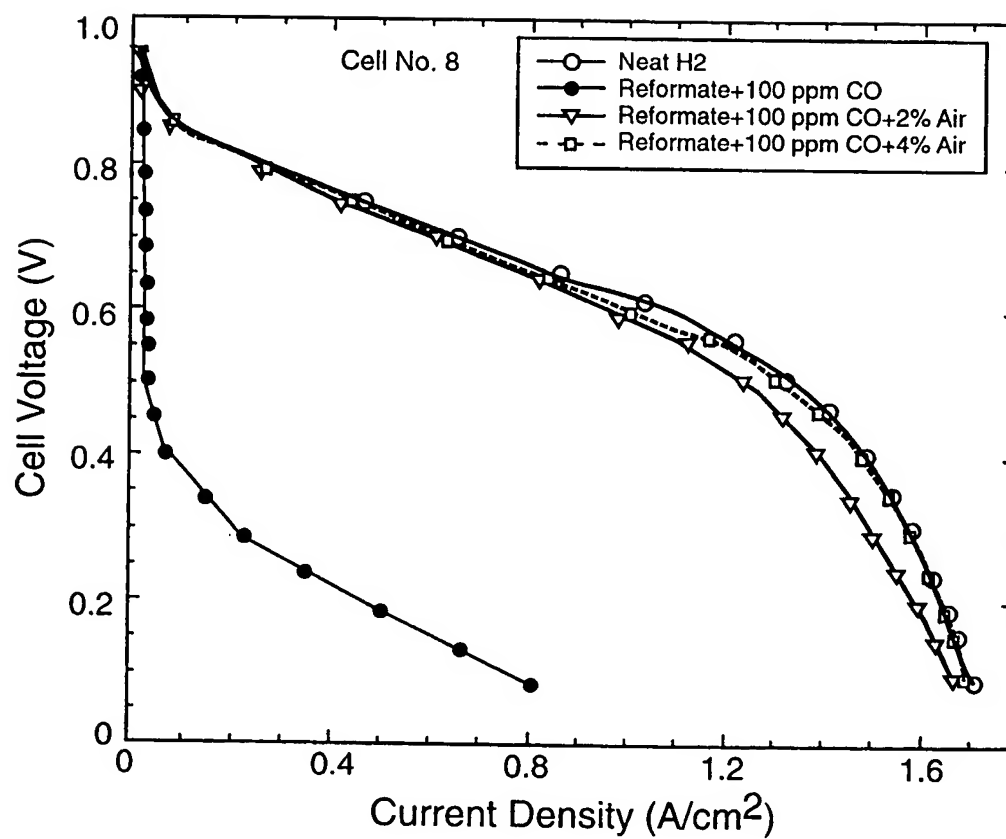**Fig. 2**

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/30115

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01M 8/02, 8/10, 4/86, 4/90, 4/92

US CL :429/18, 30, 40, 41, 44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/18, 30, 40, 41, 44, 45

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JPAB, EPAB, Derwent

search terms: catalyst, oxidat*, oxidiz*, co, carbon monoxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 9-129243 A (TOYOTA CENTRAL RES & DEV LAB INC) 16 May 1997, see abstract; Figure.	1-6
Y	DE 197 18 970 A1 (EPPLE et al) 12 November 1998, see abstract; Figure 2; col. 3, lines 36-51; col. 5, lines 20-23.	1-6
Y	US 5,482,680 A (WILKINSON et al) 09 January 1996, see Figs. 15 and 16; col. 12, line 37-col. 13, line 32.	1-6
Y	US 5,234,777 A (WILSON) 10 August 1993, see col. 1, line 24; col. 3, line 48-col. 4, line 22; Protocol I; claim 1.	1-6
Y	US 5,672,439 A (WILKINSON et al) 30 September 1997, see Figure 4; col. 6, line 61-col. 7, line 6; col. 8, lines 17-24.	1-6

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
19 FEBRUARY 2000	21 MAR 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JONATHAN CREPEAU Telephone No. (703) 308-0651

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document. with indication. where appropriate. of the relevant passages	Relevant to claim No.
P, A	US 5,863,673 A (CAMPBELL et al) 26 January 1999, see Figure 3; col. 3, lines 14-35; col. 6. lines 3-7.	1-6
A	JP 8-203537 A (MATSUSHITA ELECTRIC IND CO LTD) 09 August 1996, see abstract; Figure 2.	1-6